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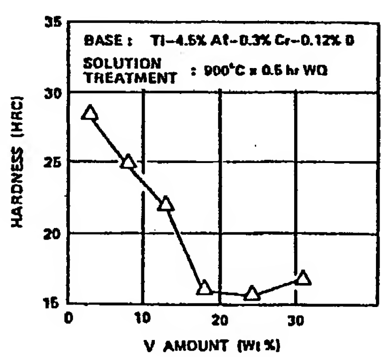
(54) **Titanium alloys.**

(57) A titanium alloy having an excellent cold workability is disclosed, which consists essentially of 8-25 wt % of V, 0.5-5 wt% of Al, less than 1.0 wt% of Cr, not more than 1.0 wt% of Fe, not more than 1.0 wt% of Mn, and the balance being substantially Ti and is used as a material for spacecrafts, aircrafts, automobiles, mechanical and structural components and so on.

FIG. 1



EP 0 202 791 A1

TITANIUM ALLOYS

This invention relates to titanium alloys, and in particular to titanium alloys having an excellent cold workability for use as materials for spacecrafts, aircrafts, automobiles, mechanical and structural components, biomaterials, goods for civilian use and so on.

Titanium alloys have a strength equal to that of steel and are light in weight, so that they have been extensively used as materials for spacecrafts and aircrafts for some time. Lately, they have begun to be used as materials for automobiles, mechanical and structural components, biomaterials, goods for civilian use and so on.

Known titanium alloys have various chemical compositions. Among them, a Ti-6Al-4V alloy is most used because it has stable mechanical properties and is easy to handle. However, this titanium alloy contains about 80% of the α-phase which has a hexagonal crystal structure having a small deformability, so that it is difficult to cold work the alloy by not less than 25%. Therefore, single phase type titanium alloys with the β-phase having a body-centered cubic crystal structure having a good cold workability are proving attractive. Examples of single β-phase type titanium alloys are Ti-11.5%Mo-6%Zr-4.5%Sn, Ti-13%V-11%Cr-3%Al, Ti-10%V-2%Fe-3%Al and the like.

However, the aforementioned conventional single β-phase type titanium alloys can be subjected to cold working at a working rate of about 70%, but have a problem in that the service life of a mould in case of cold forging is short and in case of cold drawing or cold rolling baking to the die or roll is liable to occur because the hardness of the alloys is fairly high, being more than about H_RC=30.

The invention aims to overcome the aforementioned problems and to provide single β-phase type titanium alloys having an excellent cold

workability. Furthermore, it is an object to provide such titanium alloys which, on cold forging, permit a long service life of the mould and do not cause baking to the die or roll when being cold drawn or cold rolled.

According to the invention, there is the provision of a single β-phase type titanium alloy having an excellent cold workability, comprising, on a weight percentage, 8-25% of V, 0.5-5% of Al, less than 1.0% of Cr, not more than 1.0% of Fe, not more than 1.0% of Mn, and if desired, not more than 5% in total of at least one or more than one of 0.01-3.0% of REM and 0.01-1.0% of each of Ca, S, Se, Te, Pb and Bi, and the balance being substantially Ti.

Embodiments of the invention will now be described by way of example only with reference to the accompanying drawings, wherein:

Figures 1 and 2 are graphs showing respectively the relationship between the amount of vanadium and the hardness and limit compression ratio in titanium alloys based on Ti-4.5%Al-0.3%Cr;

Figure 3 is a graph showing the relationship between the amount of aluminium and the hardness in titanium alloys based on Ti-18%V-0.3%Cr;

Figures 4a and 4b are diagrammatical views illustrating shapes of specimens used before and after a compression test, respectively;

Figure 5 is a graph showing deformation resistance and deforamtion limit of the specimen meausured by the compression test; and

Figure 6 is a graph showing the influence of ageing temperature on hardness.

The reason why the chemical composition of the single β-phase type titanium alloys having an excellent cold workability according to the

invention are limited to the above ranges is mentioned as follows.

V: 8-25%

V is a most important element according to the invention. In the titanium alloys, it is necessary substantially to render the structure into the single ß-phase for improving the cold workability. Such a single ß-phase structure is attained by adding a ß-phase stabilizing element. As the ß-phase stabilizing element, there are metallic elements such as Mo, V, Ta, Nb, Fe, Cr, Mn and the like. Among them, only Mo and V each forms a single ß-phase alloy having a low strength, while when the single ß-phase structure is formed by the addition of any of the other elements, the hardness (H_RC) exceeds 25 and the cold workability lowers. Moreover, Mo has a high melting point, poor productivity and high cost, so that it is of poor practical use.

The inventors have made many experiments on these ß-phase stabilizing elements, and have found that only V can improve the cold workability without increasing the hardness. In these experiments, there was examined, for example, the relation between the amount of V added to the Ti alloy and the hardness after the solution treatment. That is, various titanium alloys based on Ti-4.5%Al-0.3%Cr having varying V amounts were melted through button arc melting to form 100g ingots. Then, each ingot was rolled into a rod 10mm in diameter, which was subjected to a solution treatment under a condition that it was heated at 900°C for 0.5 hour and cooled with water. The hardness and cold workability were measured after the solution treatment.

In Figure 1 is shown a relation between the amount of V added to the Ti-4.5%Al-0.3%Cr alloy and the hardness after the solution treatment.

As shown in Figure 1, the hardness lowers as the amount of V added becomes larger, and the objective hardness of H_RC=not less than 25 is obtained when the addition amount is not less than 8%. The reduction

of the hardness is continued when the amount becomes not more than about 20%, and then levels out when it exceeds 20%.

Figure 2 is a graph showing the results of a compression test using a specimen 6mm in diameter and 11.5mm in length, wherein the ordinate is a limit compression ratio being a value of strain (ln[initial height (ho) / height after compression (h)]) when cracks are produced in the surface of the specimen, and shows that as the above value becomes larger, cracks are hardly produced by cold working.

As shown in Figure 2, the cold workability is enhanced in accordance with the increase of the V amount in the Ti-4.5%Al-0.3%Cr alloy.

As shown in Figures 1 and 2, the amount of V added in the titanium alloy is determined from a viewpoint of the fact that the hardness after the solution treatment is made low and the cold workability is enhanced. Particularly, the preferable amount of V is determined by the amount of Cr as a β-phase stabilizing element, from which it is limited to a range of 8-25% in the titanium alloy according to the invention. That is, as apparent from the above, when the amount of V is less than 8%, the α-phase is retained in the alloy to degrade the cold workability, while when it exceeds 25%, the age hardening is not caused and consequently high strength is not obtained in use.

Al: 0.5-5%

The single β-phase type titanium alloys are usually used after they have been subjected to a solution treatment, cold working, and age hardening treatment. In this case, the addition of Al raises the ductility after the age hardening treatment. Particularly, such an effect is well recognized at an Al amount of 0.5-3%.

On the other hand, the influence of the addition of Al on the hardness of the titanium alloys was examined. That is, various titanium alloys

based on Ti-18%V-0.3%Cr having varying Al amounts were melted through button arc melting to form 100g ingots. Each ingot was rolled into a rod 10mm in diameter, which was subjected to a solution treatment by heating at 700°C for 0.5 hour and cooling with water. The hardness after the solution treatment was measured to obtain the results shown in Figure 3.

As shown in Figure 3, it is apparent that the hardness increased as the Al amount becomes larger. However, the large amount of Al added increases only the hardness, but does not enhance the ductility.

Now, in order to provide the single β-phase type titanium alloys cheaply, it is effective to use scrap of Ti-6%Al-4%V as a starting material.

The amount of Al added is limited to a range of 0.5-5% in view of the enhancement of ductility and increase of hardness through Al addition, the production cost and the like.

Cr: less than 1.0%

Cr is a β-phase stabilizing element and is effective for rendering the crystal structure of the base into a body-centered cubic system. However, it is desirable to add Cr in an amount as small as possible in order to decrease the hardness after the solution treatment. Therefore, the amount of Cr is selected to be less than 1.0% owing to the effect of stabilizing the β-phase.

Fe: not more than 1.0%

Mn: not more than 1.0%

Fe and Mn are β-phase stabilizing elements and are effective for rendering the crystal structure of the base into a body-centered cubic

system. However, it is desirable to add each of them in an amount as small as possible in order to decrease the hardness after the solution treatment. As to the effect of stabilizing the β-phase, assuming that V is 1, Mn is 2.4, and Fe is 4.3, and both the elements are cheap, so that their composite addition brings about ecconomical merits. In this connection, each of Fe and Mn is selected to be not more than 1.0%.

REM (one or more than one of rare earth element) : 0.01-3.0%

One or more than one of Ca, S, Se, Te, Pb and Bi : 0.01-1.0% of each

At least one or more than one of REM, Ca, S, Se, Te, Pb, and Bi : not more than 5% in total

All of REM, Ca, S, Se, Te, Pb and Bi are elements effective for improving the free cutting property of the titanium alloys.

Among them, the rare earth element REM [particularly, Sc, Y and lanthanoide (atomic number : 57-71)] forms a stable compound with S, Se, Te and the like to render inclusions into granules, and is effective for improving the toughness, ductility and free cutting property. In order to obtain such an effect, REM is added in an amount of not less than 0.01%, if necessary. However, if it is too large, the corrosion resistance and strength of the titanium alloys are reduced, so that it should be limited to not more than 3.0%. Furthermore, Ca forms a stable compound with S, Se, Te and the like to control the form of the inclusions, and is effective for improving the toughness, ductility and free cutting property. In order to provide such an effect, Ca is added in an amount of not less than 0.01%. However, if the amount is too large, the corrosion resistance and fatigue strength of the titanium alloys are reduced, so that it should be limited to not more than 1.0%. And also, S, Se, Te, Pb and Bi are elements for improving the free cutting property of the titanium

alloys as described above, and each of them is added in an amount of not less than 0.01%, if necessary. However, if it is too large, the hot workability of the titanium alloys is considerably decreased, so that it is limited to not more than 1.0% of each of these elements. Moreover, if the total amount of these elements REM, Ca, S, Se, Te, Pb and Bi is too large, the corrosion resistance, strength, hot workability and so on of the titanium alloys are degraded, so that the total amount of at least one or more than one is limited to not more than 5%.

Example

A titanium alloy having a chemical composition as shown in the following Table 1 was melted in a plasma progressive casting furnace and shaped into an ingot, which was forged into a rod 50mm in diameter. This rod was subjected to a solution treatment (heating at 800°C for 0.5 hour and cooling with water) to prepare a specimen.

Then, the hardness of the specimen after the solution treatment was measured as follows, while the cutting test for the free cutting property and the compression test for the cold workability were carried out. The measurement of the hardness was performed according to Rockwell C scale. The cutting test was carried out under the conditions shown in the following Table 2 to measure a life rate of 1000mm, from which a ratio of the life rate when the conventional 6%Al-4%V-Ti alloy is 100, or a drill life rate ratio was evaluated. The compression test was performed by compressing a specimen 6mm in diameter and 11.5 mm in height (ho) to a height (h), during which a deformation resistance was measured and evaluated as a cold workability.

The measured value of the hardness and test results on the free cutting property are shown in Table 1, and the results of the compression test are shown in Figure 5.

T a b l e 1

No.	Chemical composition (wt%)														Hardness	Drill life	Remarks
	Al	V	Cr	Fe	Mn	O	Ca	S	Se	Te	Pb	Bi	REM	Ti	(HRC)	rate ratio	
1	4.5	8	0.2	0.1	0.1	0.12	-	-	-	-	-	-	-	Bal	25	130	Invention example
2	1.5	13	0.2	0.2	0.1	0.14	-	-	-	-	-	-	-	Bal	21	160	
3	1.4	24	0.3	0.1	0.1	0.22	-	-	-	-	-	-	-	Bal	18	165	
4	4.5	8	0.2	0.1	0.1	0.12	0.5	-	-	-	-	-	-	Bal	25	230	
5	1.5	13	0.07	0.2	0.2	0.12	-	0.5	-	-	-	-	1.0	Bal	22	270	
6	1.6	18	0.1	0.1	0.1	0.12	-	-	-	-	0.2	-	-	Bal	16	394	
7	1.4	24	0.05	0.1	0.1	0.12	-	-	-	-	-	0.5	-	Bal	16	420	
8	4.5	8	0.2	0.1	0.1	0.12	-	0.5	0.5	-	-	-	1.0	Bal	25	290	
9	4.5	8	0.2	0.1	0.1	0.12	-	-	-	0.5	-	-	-	Bal	25	350	
10	4.5	8	0.2	0.1	0.1	0.12	-	0.5	-	-	0.1	0.1	-	Bal	25	290	
11	4.5	8	0.2	0.1	0.1	0.12	0.5	0.5	0.5	0.5	-	-	1.0	Bal	25	320	
12	6	4	-	-	-	-	-	-	-	-	-	-	-	Bal	31	100	Comparative example
13	3.1	13	11.0	0.1	0.2	0.15	-	-	-	-	-	-	-	Bal	32	60	

Table 2

Tool	drill of SKH9 with a diameter of 5mm
Feeding rate	0.05 mm / rev
Drilled depth	20 mm
Lubricant	water soluble cutting oil

As shown in Table 1, the titanium alloys according to the invention Nos. 1-11) have the hardness H_RC= not more than 25 after the solution treatment. As apparent from the results of compression test in Figure 5, the titanium alloys according to the invention (Nos. 1-3) have a fairly small deformation resistance and have considerably lower surface cracking as compared with the conventional alloys of Ti-6Al-4V (No. 12) and Ti-13V-11Cr-3Al (No. 13). That is, the titanium alloys according to the invention (Nos. 1-3) have excellent cold workability, have a low drill life rate ratio as shown in Table 1, and have a good free cutting property. Furthermore, in case of the alloys (Nos. 4-11) containing at least one of REM, Ca, S, Se, Te, Pb and Bi, the surface cracking is apt to be somewhat caused as shown in Figure 5, but is hardly caused as compared with the conventional alloy of Ti-6Al-4V (No. 12), while the drill life rate ratio is fairly high as compared with the conventional alloys (Nos. 12, 13), so that they are excellent in not only the cold workability but also the free cutting property.

Then, the age hardening property of the titanium alloy shown in No. 7 of Table 1 was examined. The measured result is shown in Figure 6.

As shown in Figure 6, the hardness is increased by subjecting the alloy to an age hardening treatment after the solution treatment above 700°C, and in this case, the increase of the hardness is largest at the hardening temperature of 400°C. For instance, hardness in H_RC rises from 16 to 34 when the solution treating temperature is 900°C, from which it has been confirmed that the cold workability after the solution treatment is excellent and also the strength after the age hardening treatment is high. Furthermore, it has been found that when the cold working is performed after the solution treatment, the hardness after the age hardening treatment is raised only by the quantity hardened through the cold working.

As previously mentioned in detail, the single β-phase type titanium alloys according to the invention, consisting essentially of, by weight percentage of, 8-25% of V, 0.5-5% of Al, less than 1.0% of Cr, not more than 1.0% of Fe, not more than 1.0% of Mn, and if necessary, not more than 5% in total of at least one or more than one of 0.01-3.0% of REM and 0.01-1.0% in each of Ca, S, Se, Te, Pb and Bi, and the balance being substantially Ti, are excellent in the cold workability as compared with the existing alloy of Ti-6Al-4V. When being subjected to a cold working, the service life of the mould becomes longer, and also when being subjected to a cold drawing or cold rolling, baking to the die or roll is hardly produced, so that the productivity of components and articles becomes excellent. Therefore, the titanium alloys according to the invention can widely be applied to materials for spacecrafts, aircrafts, automobiles, mechanical structural components, biomaterial, goods for civilian use and so on by effectively utilizing light weight, corrosion resistance, high strength and the like of the titanium alloys. For example, the invention has an excellent effect, as a result of the light weight, strong toughness and low cost due to the good productivity of the titanium alloys, when they are used for valves, valve retainers, valve springs in automotive engine, frames of pairs of spectacles and the like.

CLAIMS:

1. A titanium alloy having an excellent cold workability, consisting essentially of, by weight percentage of, 8-25% of V, 0.5-5% of Al, less than 1.0% of Cr, not more than 1.0% of Fe, not more than 1.0% of Mn, and the balance being substantially Ti.

2. A titanium alloy according to Claim 1, wherein said alloy has a hardness of H_RC= not more than 25 after solution treatment.

3. A titanium alloy having an excellent free cutting property and cold workability, consisting essentially of, by weight percentage of, 8-25% of V, 0.5-5% of Al, less than 1.0% of Cr, not more than 1.0% of Fe, not more than 1.0% of Mn, not more than 5% in total of at least one or more than one of 0.01-3.0% of REM and 0.01-1.0% in each of Ca, S, Se, Te, Pb and Bi, and the balance being substantially Ti.

4. A titanium alloy according to Claim 3, wherein said alloy has a hardness of H_RC= not more than 25 after solution treatment.

FIG. 1

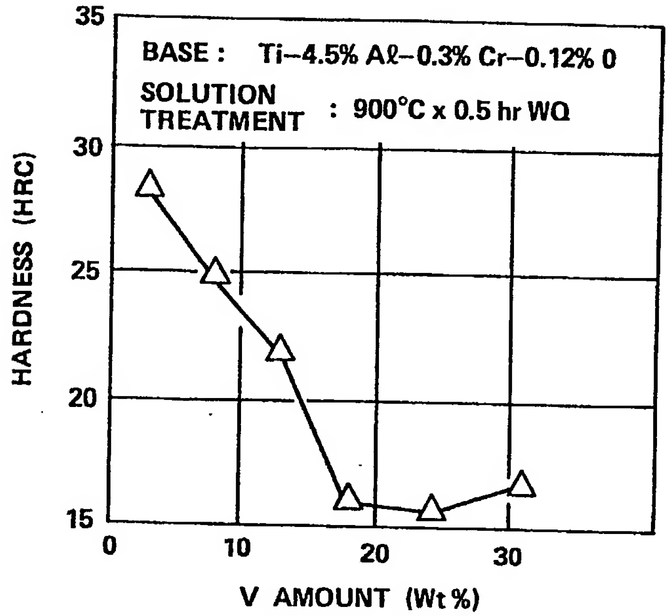

BASE : Ti–4.5% Aℓ–0.3% Cr–0.12% O
SOLUTION TREATMENT : 900°C x 0.5 hr WQ
HARDNESS (HRC)
35
30
25
20
15
0
10
20
30
V AMOUNT (Wt %)

FIG. 2

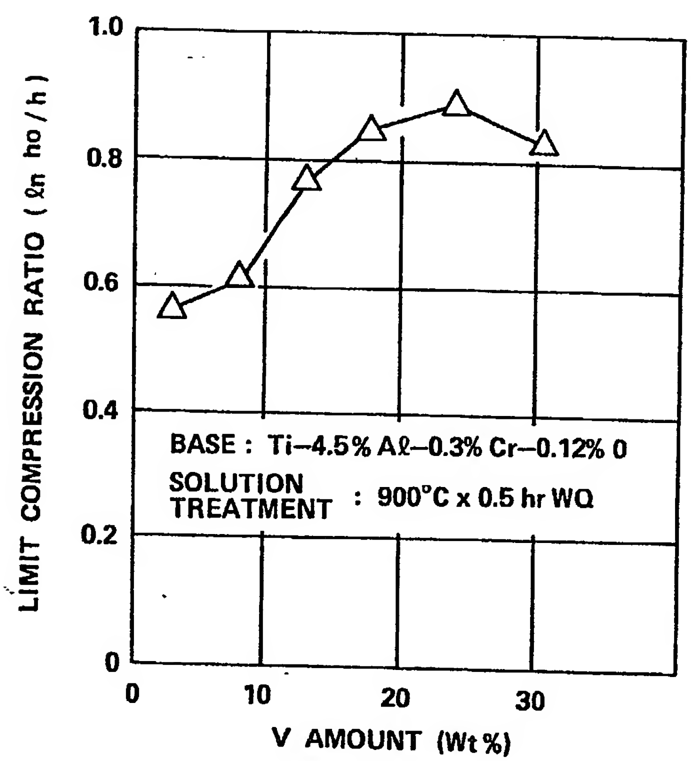

LIMIT COMPRESSION RATIO (ℓn ho / h)
1.0
0.8
0.6
0.4
0.2
0
BASE : Ti–4.5% Aℓ–0.3% Cr–0.12% O
SOLUTION TREATMENT : 900°C x 0.5 hr WQ
0
10
20
30
V AMOUNT (Wt %)

FIG.3

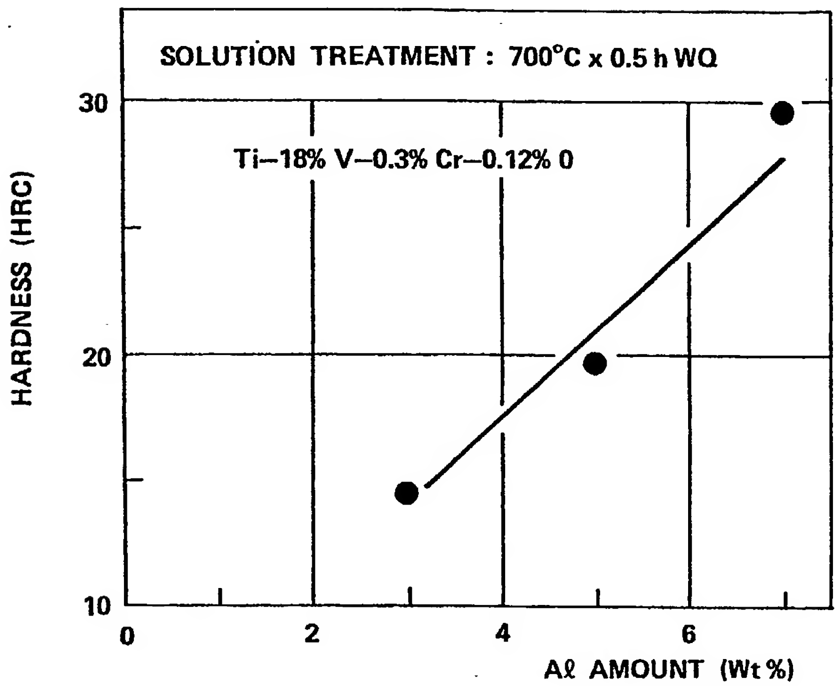

SOLUTION TREATMENT : 700°C x 0.5 h WQ
Ti–18% V–0.3% Cr–0.12% O
HARDNESS (HRC)
30
20
10
0
2
4
6
Aℓ AMOUNT (Wt %)

FIG.6

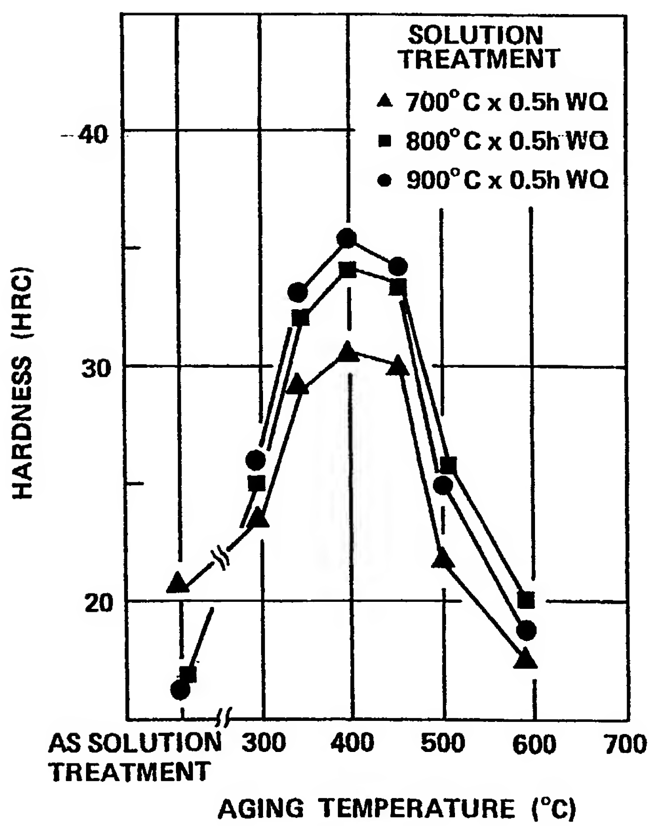

SOLUTION TREATMENT
▲ 700°C x 0.5h WQ
■ 800°C x 0.5h WQ
● 900°C x 0.5h WQ
HARDNESS (HRC)
40
30
20
AS SOLUTION TREATMENT
300
400
500
600
700
AGING TEMPERATURE (°C)

FIG.4

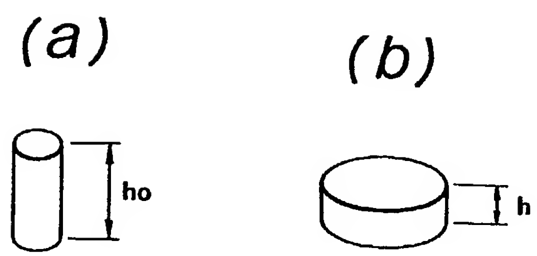
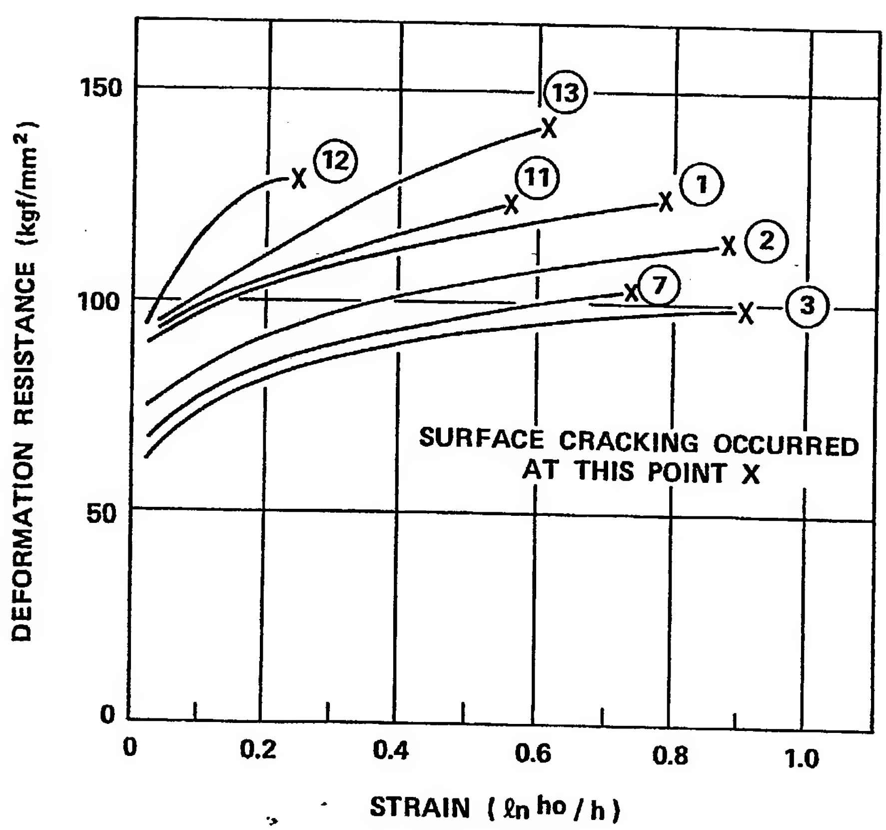

(a)
(b)
ho
h

FIG.5


150
100
50
0
0
0.2
0.4
0.6
0.8
1.0
DEFORMATION RESISTANCE (kgf/mm²)
STRAIN (ℓn ho / h)
13
12
11
1
2
7
3
X
SURFACE CRACKING OCCURRED
AT THIS POINT X

0202791

European Patent Office

EUROPEAN SEARCH REPORT

Application number

EP 86 30 3107

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int Cl 4)
X	US-A-2 864 697 (BUSCH et al.) * Claims 1-6 * & GB - A - 823 420, & FR - A - 1 216 591	1	C 22 C 14/00
A	GB-A-1 124 962 (IMPERIAL METAL INDUSTRIES KYNOCH LTD.) * Claims 1,3 *	1	
A	GB-A- 911 148 (CRUCIBLE STEEL INTERNATIONAL) * Claims 1-4 *	1	

TECHNICAL FIELDS SEARCHED (Int. Cl 4)

C 22 C 14/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	07-08-1986	LIPPENS M.H.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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L : document cited for other reasons

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